Latent superconductivity in doped manganites

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We analyze effective Hamiltonian of ferromagnetic half metal phase of doped manganites and find a latent *d-wave spin triplet* superconductivity. Spin triplet state for a d-wave pair is enabled by orbital degrees of freedom. This high Tc superconductivity is, however, kept dormant by some intrinsic strong cooper pair breaking processes. Low T anomalies such as i) long distance superconducting proximity effects into manganites, ii) pseudogaps in tunneling, ARPES and iii) nodal quasi particles and absence of bilayer splitting in ARPES in bilayer manganite get natural and qualitative explanation. Some consequences of our orbital pairing superconductivity are pointed out.

Manganites host a variety of thermodynamic phases and exhibit rich physics and phenomena arising from an interplay of electronic and orbital degrees of freedom[1]. The spin, charge, orbital and lattice degrees of freedom are tied in a complex fashion, leading to remarkable control of electron transport by magnetic or electric fields, in phenomena such as colossal magnetoresistance or electroresistance effects. These make manganites special and exciting from technological point of view. From basic science point of view, manganites are formidable, compared to its less complex cousin, high T_c copper oxides

In many transition metal oxides, orbital angular momentum of d-electrons are only partially quenched and some orbital degeneracy remains. Kugel and Khomskii[2] pioneered important theoretical studies in this front. In doped oxides with strong electron correlations, instead of undergoing a cooperative Jahn-Teller distortion and orbital order, electrons tend to quantum fluctuate among degenerate orbitals, resulting in a state with disordered orbital occupancy. This state is called 'orbital liquid'[3]. In the recent past, orbital fluctuation has been studied both theoretically and experimentally, leading to deeper insights into magnetic and electrical properties of some transition metal oxides, including violation[4] of celebrated Goodenough-Kanamori rules.

On the experimental front, fully polarized ferromagnetic manganite family of metals exhibit anomalous features such as large Drude width in optical conductivity[5], pseudo gap[6, 7, 8], absence of quasi particle peak[9], nodal quasi particles in photoemission studies[10] and anomalous superconducting proximity effects[11] at low temperatures. Various theoretical efforts[12] have attempted to explain the rich variety of properties of manganites, occuring at small and high energy scales, using double exchange and Jahn-Teller polaron mechanisms, in the ferro and paramagnetic phases. However, there is a need for an unified explanation of the above low T and low energy, 1 to 10 meV anomalies in the ferromagnetic phase.

The aim of the present article is to explain qualitatively low energy anomalies in a natural and unified fashion, for manganites and related systems. We suggest that in the fully spin polarized low T metallic phase there is a 'latent high T_c superconductivity'. The order parameter is a d-wave spin triplet. The enhanced superconducting correlations arise from strong electron correlation induced pairing among orbital degrees of freedom between two electrons with parallel spins. Orbital degree of freedom offers a possibility to have *d-wave spin triplet*, still maintaining the overall antisymmtry of the many electron wave function.

After specializing the model Hamiltonain of manganite to fully polarized ferromagnetic phase, we isolate a major part of it. It is a large repulsive U Hubbard model (or its variant t-J model), with spin-half degree of freedom replaced by orbital (pseudospin-half) degree of freedom. This piece has global SU(2) symmetry in pseudospin space. Using an RVB theory analysis[13, 14, 15, 16], we find that this part of the model for manganite exhibits $d_{x^2-y^2}$ or $d_{y^2-z^2}$ or $d_{z^2-x^2}$ wave high T_c pseudospin (orbital) singlet superconductivity. The remaining nonsymmetric SU(2) part are strong pair breakers and destroy long range superconducting order.

We explain some experimental anomalies in a qualitative fashion using our theory. We end with some predictions and discussions.

Our finding also implies a generic possibility in oxides that *electrons overcome single particle kinetic energy frustraion imposed by strong mutual coulomb repulsions, by pair delocalisation in either spin or orbital channels.* It is likely that some of the known charge order correlations in manganites and other systems are finite momentum condensates of cooper pairs of the type we have suggested.

We start with the effective Hamiltonian[18, 19] for doped manganite $La_{1-x}Sr_xMnO_3$. In the Mott insulating manganite $LaMnO_3$ trivalent Mn^{3+} has an electronic configuration $3d^4$. In a cubic crystal field the 3d level is split into doubly degenerate e_g and triply denerate t_{2g} levels. Three of the four parallel spins fill the t_{2g} levels and the fourth occupies one of the e_g doublet. Hund coupling gives a (maximal) spin 2 for Mn^{3+} ion. In the doped metallic state Hund coupling favors a fully polarized ferromagnetic ground state. In view of the large Hubbard U,

which discourages charge fluctuation into Mn^{2+} state, *the fully polarized ferromagnetic ground state is not a simple Slater determinant state. It is a correlated quantum state.* This is clearly suggested by the effective large U Hubbard Hamiltonian, containing a part symmetric and rest non-symmetric, in an orbital index, as explained below :

$$H_{\rm FM} = H_{\rm S} + H_{\rm NS}$$
$$H_{\rm S} = -t \sum_{\langle {\rm ij}\rangle \tau=\pm} c^\dagger_{i\tau\uparrow} c_{j\tau\uparrow} + h.c. + \frac{U}{2}\sum_i n_{i+\uparrow} n_{i-\uparrow} \quad (1)$$
$$H_{\rm NS} = -t \sum_{\langle ij\rangle} e^{i\theta_{ij}} c^\dagger_{i+\uparrow} c_{j-\uparrow} + h.c. \quad (2)$$

As we are in the fully polarized ferromagnetic subspace, the t_{2g} core spin degree of freedom and Hund coupling do not appear explicitly in the Hamiltonian. The subscript $\tau = \pm$ refers to two complex combination of e_g orbitals: $|d_{x^2-y^2}\rangle \pm$ i $|d_{3z^2-r^2}\rangle$. As discussed by Feiner and Oles[19], this complex combination gives a charge density with full cubic symmetry. This combination is a more natural atomic basis to discuss ferromagnetic manganite, around x $\approx$ 0.3, where the system has a cubic symmetry and is believed to be an orbital liquid, with equal occupancy of the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals. This is inferred, for example, through an isotropic spin wave spectrum in neutron scattering results[20].

Another advantage of this basis is that near neighbor hopping matrix elements have the same strength for both diagonal and off diagonal terms. However, the off diagonal term has extra phases, $\theta_{ij} = \pm\frac{2\pi}{3}, 0$ for hopping along a,b and c-axis, as discussed in detail by Feiner and Oles[19].

For manganites band parameters estimates[18, 19] are: Hubbard U $\approx$ 6 eV and t$\approx$ 0.4 eV. It is a large U repulsive Hubbard model, with a key difference of an off diagonal hopping term in the pseudo spin index τ. That is, $H_{\rm S}$ (eqn.1) has global SU(2) symmetry in pseudo spin space; $H_{\rm NS}$ (eqn.2) does not have global SU(2) symmetry.

This and similar model has been studied in great detail recently[19]. What we offer is a new qualitative analysis and insights that has phenomenological support, as shown below.

The SU(2) symmetric part H_S is the standard large U Hubbard model away from half filling. RVB theory[13, 14] suggests that antiferromagneic superexchange interaction generated by virtual fluctuations into doubly occupied states lead to spin singlet correlations and superconductivity. In our case it gives a superconducting ground state with cooper pairs made of orbital pseudospin singlets and physical spin triplets $|\uparrow\uparrow\rangle$. The corresponding electron pair is created by an operator,

$$b^\dagger_{ij} \equiv \frac{1}{\sqrt{2}}(c^\dagger_{i+\uparrow} c^\dagger_{j-\uparrow} - c^\dagger_{i-\uparrow} c^\dagger_{j+\uparrow}) \quad (3)$$

A very successful variational ground state for the SU(2) symmetric part of the Hamiltonian is the d-wave superconducting state, containing a Gutzwiller-Jastrow factor which discourages double occupancy: in our present case it is a spin triplet, pseudo spin singlet d-wave superconducting state:

$$|G\rangle = \prod_i (1 - g n_{i+\uparrow} n_{i-\uparrow}) \prod_k (u_k + v_k c^\dagger_{-k+\uparrow} c^\dagger_{k-\uparrow})|0\rangle \quad (4)$$

The cooper pair function $\frac{v_k}{u_k}$ has $d_{x^2-y^2}$ type symmetry. The projection factor g = 1 - O($\frac{t}{U}$).

As we have a 3 dimensional system, there are three degenerate states of the d-wave superconductor order parameter: $d_{x^2-y^2}$, $d_{y^2-z^2}$ and $d_{z^2-x^2}$. In the latent superconducting phase, all three pairing will appear with equal probability, as fluctuating domains of superconducting pair correlations. For the case of bilayer manganite, $La_{2-x}Sr_{1+x}Mn_2O_7$, the intrinsic 2D character will pickup only the $d_{x^2-y^2}$ pairing correlations. The magnitude of the superconducting gap depends on doping. For manganites in the good metallic ferromagneic state x $\approx$ 0.3, we are in the overdoped regime, as compare to layered cuprates.

This seemingly robust long range superconducting order is not stable against pair breaking processes represented by the off diagonal hopping term $H_{\rm NS}$. This term flips the pseudo spin and is analogous to a 'spin-orbit' (pseudospin-orbit) coupling, but strong. A pseudo spin singlet electron pair has a finite probability of becoming pseudo spin triplet spontaneously. In an analysis, similar to pair breaking theory in BCS theory, we find that superconducting Tc gets suppressed to zero.

It is somewhat straight forward to see that the strong pair breaking destroys d-wave superconductivity. However, it is difficult to quantify the surviving pairing correlations. The problem is hard and has some similarity to issues of pairing correlations in the spin gap phase in cuprates.

Jahn-Teller coupling leads to cooper pair breaking, as outlined below. Coupling of charge of an e_g electron to c-axis (or a or b axis) distortion of oxygen octahedra lifts two fold e_g degeneracy, as represented by the electron-lattice interaction Hamiltonian:

$$H_{\rm JT} = g_{\rm JT} \sum_i (c^\dagger_{i1\uparrow} c_{i1\uparrow} - c^\dagger_{i2\uparrow} c_{i2\uparrow})\ \hat{q}_i \quad (5)$$

Here the subscript 1,2 refer to the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals; $\hat{q}_i$ is the c-axis distortion variable and Jahn-Teller coupling constant $g_{\rm JT} \sim 10$ eV/Au. After transforming to the complex d $\pm$ id basis, it becomes an off diagonal scattering term, that flips the pseudo spin:

$$H_{\rm JT} = g_{\rm JT} \sum_i (c^\dagger_{i+\uparrow} c_{i-\uparrow} + c^\dagger_{i-\uparrow} c_{i+\uparrow})\ \hat{q}_i \quad (6)$$

Thus the major Jahn-Teller coupling does not conserve the psuedo spin and hence acts like a pair breaker for the pseudo spin singlet cooper pairs. However, coupling to some specific inter octahedral distortions may favour local bond singlets of pseudospins.

As we increase T, thermal spin waves (goldstone modes) are produced. The more the occupancy of the spin wave modes, the more we go out of the ferromagnetic Hilbert space. The pseudo spin singlet stabilizing process is compatible with Hund coupling; that is, once neighboring spins are antiparallel, Hund coupling discourages charge hopping and hence pseudo spin 'superexchange'. Thus electron spin reversals reduce the pseudospin singlet or superconducting correlation.

Having suggested a possibility of enhanced superconducting correlation in the ferromagnetic metallic doped manganites, we will discuss known anomalies in the present light. They seem to fall in place, at a qualitative level.

When a normal metal is in contact with a singlet or triplet superconductor, proximity effect[21] is induced over a length scale given by $\xi \sim \sqrt{\frac{\hbar v_F \ell_F}{\pi kT}}$ (dirty limit) or $(\frac{\hbar v_F}{6\pi kT})$ (clean limit). Here ℓ_F is the electron mean free path at the fermi surface. The diverging proximity effect, reflects divergent singlet and triplet pair susceptibility of a free fermi gas as $T \to 0$. If the metal is replaced by a half metallic ferromagnet (LCMO) and the superconductor by a singlet superconductor (YBCO), singlet pair response in the metal is no longer divergent and the proximity length scale becomes $\xi \sim \sqrt{\frac{\hbar v_F \ell_F}{\pi E_{\rm ex}}} < 1$ nm, a non divergent quantity at low temperatures. This is because a low energy spin singlet cooper pair is incompatible with a ferromagnetic half metal, where the exchange splitting $E_{\rm ex}$ makes down spin energy very high. However, in some hetrostructurers, supercurrent between singlet superconductors is seen to flow through spin polarized ferromagnetic manganitic layers[11] of large thickness of 20 to 100 nm. This is an anomaly, unexpected in a dirty metal like manganite.

It has been suggested[22] that at the interface there is a conversion of spin singlet to triplet cooper pairs through spin flip processes as well as spin rotation accompanying reflection of electron[23] by spatially varying exchange field across the interface. Spin triplet is compatible with a fully polarized ferromagnetic state; in principle this induced triplet pair correlation in the vicinity of the interface is capable of extending into ferromagnetic half metal, by standard proximity effect. However, ferromagnetic manganite is not a standard fermi liquid metal[24]; electrons undergo strong scattering through electron-electron and electron-phonon scattering. This is evident in optical conductivity, for example, where one sees an anomalously large Drude width[5]. We cannot use standard proximity theory of normal metals. We suggest that an enhanced orbital d-wave pairing and availability of the new orbital channel might cause the anomalous proximity effect, as argued below.

An electron quasiparticle from normal metal undergoes Andreev reflection, at the superconductor-normal metal interface and becomes a hole with opposite spin:

$|\mathbf{k}\uparrow\rangle_{\rm e} \to |-\mathbf{k}\downarrow\rangle_{\rm h}$. This creates an Andreev bound state and thereby an anomalous pair amplitude gets built inside the normal metal between two superconductors. Andreev bound state carries the Josephson current and creates proximity effect. We suggest the following Andreev reflection process for our superconductor- manganite metal interface:

$$|\mathbf{k}\uparrow +\rangle_{\rm e} \to |-\mathbf{k}\uparrow -\rangle_{\rm h} \tag{7}$$

That is, an electron with upspin ($\uparrow$) and pseudo spin $\tau = +$ gets reflected at the boundary to become a hole with upspin ($\uparrow$) and pseudo spin $\tau = -$. In a spin singlet superconductor electron reverse the spin in an Andreev reflection. However, as mentioned before, appearance of a finite exchange field on one side of the interface removes the global spin SU(2) symmetry. That is why the process represented by equation (5) will occur with a finite probability that is related to spin rotation by exchange field as well as spin flip scattering by magnetic impurities. In a similar fashion there are processes that causes pseudospin flip, required by orbital singlet pairing in manganite.

Qualitatively, making use of the existing latent superconductivity in manganite, the above Andreev reflection builds a stronger spin triplet, orbital singlet anomalous pair amplitude and longer proximity effect, than expected in a dirty metallic state of manganite.

Different pseudogaps have been seen in STM, tunneling and ARPES [6, 7, 8, 9], over two energy scales, one around 200 meV and the other[7] around 15 meV. The origin of the very large gaps in tunnelling and STM is not very clear. We suggest that the smaller pseudogap seen in Pb-manganite tunnelling[8] corresponds to our orbital pairing and a gap of 15 meV is consistent with t, U and a large doping density for manganites.

Following earlier studies[9], a recent ARPES[10] shows the following striking phenomena in bilayer $La_{2-x}Sr_{1+x}Mn_2O_7$ at very low energy scales, of the order of 10 meV or less: i) carriers are strongly scattered at the fermi surface, electron spectral weight is strongly suppressed, resembling the normal state pseudogap phase of doped cuprates, ii) a quasi particle type structure emerge, surprisingly in the nodal (0.0)-(π,π) direction in k-space, once again resembling the pseudo gap phase of layered cuprates and iii) absence of bilayer splitting.

At a qualitative level all the above three anomalies become less anomalous and somewhat natural, in the light of our latent superconductivity with $d_{x^2-y^2}$ symmetry in bilayer manganite. In the RVB theory, nodal quasi particles reflect persistence of d-wave superconducting correlations, nodal Bogoliubov like quasi particle excitations

and spin singlet pairing into normal state. The low temperature part of the pseudo gap region is where anomalous Nernst signal and local superconductivity, sufficient to support long lived vortices are seen. Above this region, in the high temperature pseudo gap region we have spinon pairing. It will be important to get further information experimentally on the pseudo gap phase in manganite and its bilayer version, looking for some key similarities with cuprates.

Absence of bilayer splitting is related, in our proposal, to 'c-axis confinement', well known in cuprates[25] However, in $La_{2-x}Sr_{1+x}Mn_2O_7$ bare c-axis matrix element (within a bilayer) has same magnitude as the ab-plane one, unlike bilayer cuprates, where it is small by an order of magnitude. This makes the confinement in bilayer manganites even more striking and special.

The strong coupling to phonon and dynamical Jahn-Teller phenomena must be playing important role in manganites even in the ferromagnetic metallic phase, but at higher energy scales $\sim$ 100 meV. What we have suggested is that very low energy features such as anomalous proximity effects and presence of nodal quasiparticles are governed mostly by strong correlation physics and superconducting pairing correlations advocated in the present paper.

Some interesting consequences of our proposals are: i) orbital singlet correlation with d-wave symmetry will give rise to a pseudospin-1, 'orbiton' excitation[26] (similar to 41 meV resonance in cuprates) at wave vectors (π, π, π) in manganites and at (π, π) in bilayer manganite. ii) Strain and pressure control of orbital fluctuation: epitaxial strain, for example, is like to have strong effect on the anomalous proximity effect and iii) Charge 2e pairing in the latent superconducting state is likely to leave its signature in noise experiments in nano manganite systems.

The pseudospin symmetry breaking term H_{NS} has no independent parameter. Because of this we have no separate experimental control over the pair breaking processes.

In conclusion, using a body of already existing theoretical and experimental insights in cuprates and manganites, we have made a novel proposal. It will be interesting to develop our theoretical proposal further and study experimental consequences. The physics we have advocated for 3D manganites is likely to have some key common features with CrO_2, another remarkable half metal and perhaps other oxides.

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